

Cd(II) and Zn(II) Complexes Containing *N,N'*-Bidentate *N*-(Pyridin-2-ylmethylene)cyclopentanamine: Synthesis, Characterisation and Methyl Methacrylate Polymerisation

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The reaction between $[\text{CdBr}_2 \cdot 4\text{H}_2\text{O}]$ and anhydrous $[\text{ZnCl}_2]$ with *N,N'*-bidentate *N*-(pyridin-2-ylmethylene)-cyclopentanamine (**impy**) in ethanol yields dimeric $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ and monomeric $[(\text{impy})\text{ZnCl}_2]$ complexes, respectively. The X-ray crystal structure of Cd(II) and Zn(II) complexes revealed that the cadmium atom in $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ and zinc in $[(\text{impy})\text{ZnCl}_2]$ formed a distorted trigonal-bipyramidal and tetrahedral geometry, respectively. Both complexes showed moderate catalytic activity for the polymerisation of methyl methacrylate (MMA) in the presence of modified methylaluminumoxane (MMAO), with poly-methylmethacrylate (PMMA) syndiotacticity of about 0.70.

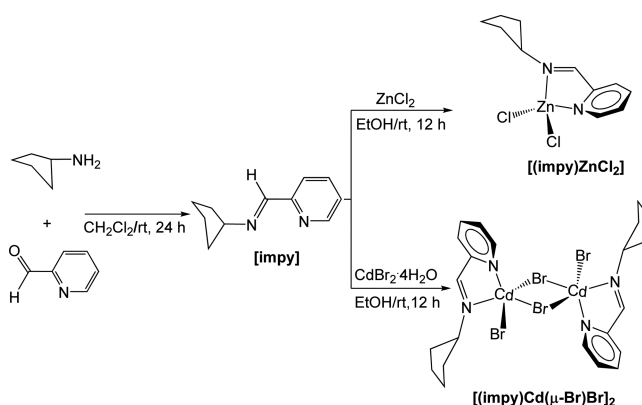
Key Words : Pyridyl-imines, Dimeric cadmium(II) complex, Zinc(II) complex, Methyl methacrylate (MMA), Syndiotacticity

Introduction

Transition metal complexes containing ancillary ligands, pyridyl-imines and *N*-substituted 2-iminoalkylpyridines have been applied for synthetic, spectroscopic and kinetic studies,¹⁻¹⁰ photoluminescence and photochemistry,¹¹ as catalysts for organic transformation,¹²⁻¹⁸ electrochemistry,¹⁹⁻²¹ bioinorganic chemistry,^{22,23} supramolecular chemistry,^{24,25} molecular magnetism²⁶⁻²⁹ and olefin polymerisation.³⁰⁻⁴⁴ In contrast, poly(methylmethacrylate) (PMMA) is a universal polymer with optical applications. In general, a higher glass transition temperature (T_g) represents a higher optical quality and increased syndiotacticity of PMMA. On the other hand, isotactic PMMA, however, which is commercially produced using conventional radical processes, has a T_g around 65 °C. However, radical-mediated polymerisation of methyl methacrylate (MMA) cannot achieve an enough high T_g or high content of syndiotacticity in PMMA. Thus, studies on non-radical-mediated MMA polymerisation, which able to produce a higher T_g up to 140 °C, have been performed, and some transition metal complexes have successfully been applied to this process.⁴⁵⁻⁵³ Recently, we explored the development of transition metal complexes as catalysts for homogeneous polymerisation of MMA to produce syndiotactic PMMA. Although the ligand **impy** has been applied to rhenium, copper, palladium and platinum complexes, rhenium and copper complexes did not utilized as catalyst for MMA polymerisation.^{4,54,55} Previously, we reported the palladium and platinum complexes with *N*-cyclopentyl-1-(pyridin-2-yl)methanimine (**impy**), in which Pd(II) complex demonstrated a very high activity for MMA polymerisation.⁵⁴ Thus, we have prepared zinc and cadmium complexes containing

the **impy** to get the higher activity than Pd(II) complexes for the MMA polymerisation. The **impy** was obtained from the condensation reaction between cyclopentylamine and 2-picolylcarbaldehyde in dichloromethane (Scheme 1). Dimeric $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ (88%) and monomeric $[(\text{impy})\text{ZnCl}_2]$ (96%) complexes were obtained from **impy** with $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ and anhydrous ZnCl_2 , respectively, in anhydrous ethanol. ¹H-NMR peaks of both complexes were shifted to low field by approximately δ 0.3 compared with **impy**, while ¹³C-NMR peaks of the both complexes were shifted to low field by approximately δ 6 compared with ligand.

A single crystal suitable for X-ray analysis was obtained from diethyl ether diffusion in DMF for $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ and acetone for $[(\text{impy})\text{ZnCl}_2]$ solution. Crystal data and structure refinement of $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ and $[(\text{impy})\text{ZnCl}_2]$ are listed in Table 1. ORTEP drawings of the



Scheme 1. Synthesis of ligand (**impy**) and complexes $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ and $[(\text{impy})\text{ZnCl}_2]$.

Table 1. Crystal data and structural refinement for $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ and $[(\text{impy})\text{ZnCl}_2]$

	$[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$	$[(\text{impy})\text{ZnCl}_2]$
Empirical formula	$\text{C}_{22}\text{H}_{28}\text{Br}_4\text{Cd}_2\text{N}_4$	$\text{C}_{11}\text{H}_{14}\text{Cl}_2\text{N}_2\text{Zn}$
Formula weight (amu)	892.92	310.51
Temperature (K)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073
Crystal system, Space group	Triclinic, P_1	Monoclinic, $P2_1/c$
Unit cell dimensions		
a (Å) & α (°)	7.7106(8) & 104.213(2)	9.5797(6) & 90
b (Å) & β (°)	9.7510(11) & 105.339(2)	18.0343(10) & 114.6850(10)
c (Å) & γ (°)	9.8866(11) & 97.259(2)	8.2160(5) & 90
Volume (Å ³)	680.21(13)	1289.71(13)
Z , Calculated density (Mg/m ³)	4, 2.180	4, 1.599
μ (mm ⁻¹)	7.455	2.292
$F(000)$	424	632
Crystal size (mm)	0.29 × 0.28 × 0.14	0.31 × 0.21 × 0.15
θ Range (°)	2.20–28.28	2.26–28.29
Limiting indices	$-10 \leq h \leq 9; -12 \leq k \leq 12; -13 \leq l \leq 10$	$-12 \leq h \leq 10; -23 \leq k \leq 24; -7 \leq l \leq 10$
Reflections collected/ unique	5030/3304 [R(int) = 0.0240]	9347/3186 [R(int) = 0.0300]
T_{max} & T_{min}	0.4217 & 0.2211	0.7249 & 0.5368
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3304 / 0 / 146	3186 / 0 / 145
Goodness-of-fit on F^2	1.287	1.171
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0611, wR_2 = 0.1296$	$R_1 = 0.0356, wR_2 = 0.0626$
R indices (all data)	$R_1 = 0.1061, wR_2 = 0.2137$	$R_1 = 0.0700, wR_2 = 0.1043$
$\Delta\rho_{\text{max}}$ and $\Delta\rho_{\text{min}}$ (e.Å ⁻³)	2.720 and -5.054	1.020 and -0.834

complexes are shown in Figure 1 ($[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$) and Figure 2 ($[(\text{impy})\text{ZnCl}_2]$). The selected bond lengths and angles were listed in Table 2.

The bond lengths of Cd–N_{pyridine} and Cd–N_{imine} in $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ were 2.330(11) Å and 2.358(11) Å, respectively. In general, the bond lengths of Pd–N_{pyridine} were shorter than those of Pd–N_{imine} due to the different basicity of imine and pyridine moieties. However, those in $[(\text{impy})\text{-}$

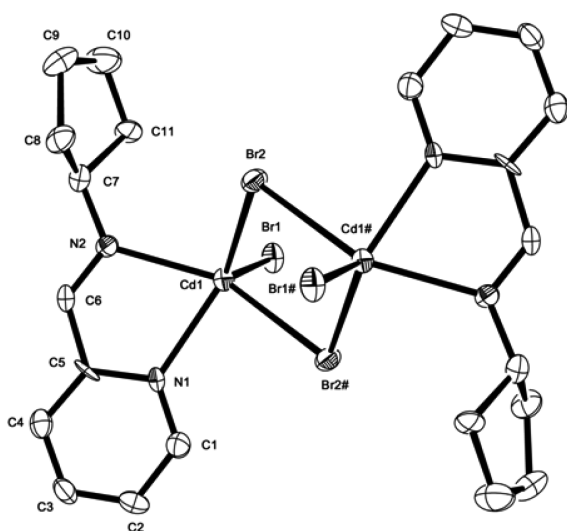


Figure 1. Molecular structure of $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ with thermal ellipsoids at 50% probability. The hydrogen atom was omitted for clarity.

$\text{ZnCl}_2]$ were 2.083(3) Å and 2.068(3) Å, respectively. The double bond of imine N(2)–C(6) of 1.288(17) Å ($[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$) and 1.277(5) Å ($[(\text{impy})\text{ZnCl}_2]$) were in the range of accepted carbon–nitrogen double bonds. The C(5)–C(6) bond distance of $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$ and monomeric $[(\text{impy})\text{ZnCl}_2]$ was 1.455(19) Å and 1.475(6) Å, respectively, reflecting delocalised π -electrons. In $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}]_2$, the Cd–Br_{terminal} bond [2.5700(18) Å] was shorter than the two Cd–Br_{bridge} bonds [2.6711(17) Å and 2.7786(17) Å]. The angles of N(1)–Zn–N(2) and Cl(1)–Zn–Cl(2) in $[(\text{impy})\text{ZnCl}_2]$ were 80.63 (14)° and 115.41(5)°, respectively, indicative of a distorted tetrahedral geometry. The N(1)–Cd(1)–N(2), N(1)–Cd(1)–Br(2#), Br(1)–Cd(1)–Br(2#), Br(1)–

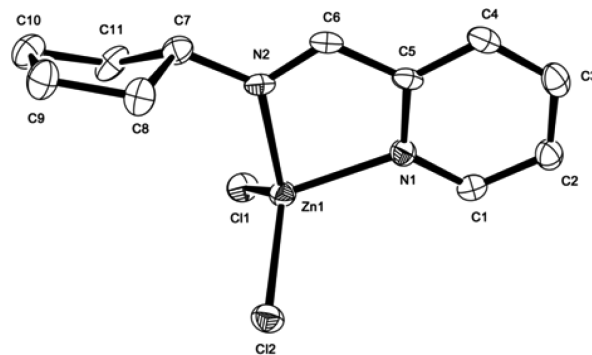


Figure 2. Molecular structure of $[(\text{impy})\text{ZnCl}_2]$ with thermal ellipsoids at 50% probability. The hydrogen atom was omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) of [(*impy*)Cd(μ -Br)Br]₂ and [(*impy*)ZnCl]₂

[(<i>impy</i>)Cd(μ -Br)Br] ₂		[(<i>impy</i>)ZnCl] ₂	
Bond lengths (Å)	Bond angles (°)	Bond lengths (Å)	Bond angles (°)
Cd(1)-N(1) 2.330(11)	N(1)-Cd(1)-N(2) 71.9(4)	Zn(1)-N(1) 2.083(3)	N(2)-Zn(1)-N(1) 80.63(14)
Cd(1)-N(2) 2.358(11)	N(1)-Cd(1)-Br(1) 108.6(3)	Zn(1)-N(2) 2.068(3)	N(2)-Zn(1)-Cl(2) 119.89(10)
Cd(1)-Br(1) 2.5700(18)	N(2)-Cd(1)-Br(1) 103.4(3)	Zn(1)-Cl(2) 2.2149(12)	N(1)-Zn(1)-Cl(2) 109.47(10)
Cd(1)-Br(2) 2.6711(17)	N(1)-Cd(1)-Br(2) 135.9(3)	Zn(1)-Cl(1) 2.2155(12)	N(2)-Zn(1)-Cl(1) 113.46(10)
Cd(1)-Br(2#) 2.7786(17)	N(2)-Cd(1)-Br(2) 94.7(3)	N(1)-C(1) 1.326(5)	N(1)-Zn(1)-Cl(1) 112.69(10)
Br(2)-Cd(1#) 2.7786(17)	Br(1)-Cd(1)-Br(2) 115.43(6)	N(1)-C(5) 1.355(5)	Cl(2)-Zn(1)-Cl(1) 115.41(5)
N(1)-C(1) 1.335(19)	N(1)-Cd(1)-Br(2#) 87.8(3)	N(2)-C(6) 1.277(5)	C(1)-N(1)-Zn(1) 129.9(3)
N(1)-C(5) 1.361(17)	N(2)-Cd(1)-Br(2#) 150.3(2)	N(2)-C(7) 1.463(5)	C(5)-N(1)-Zn(1) 111.4(3)
N(2)-C(6) 1.288(17)	Br(1)-Cd(1)-Br(2#) 103.58(6)	C(5)-C(6) 1.475(6)	Zn(1)-N(2)-C(6) 113.1(3)
N(5)-C(6) 1.455(19)	Br(2)-Cd(1)-Br(2#) 84.76(5)	C(1)-C(2) 1.380(6)	C(7)-N(2)-Zn(1) 127.3(3)

Cd(1)-Br(2), N(2)-Cd(1)-Br(2), and Br(2)-Cd(1)-Br(2#) angles for the complex [(*impy*)Cd(μ -Br)Br]₂ were 71.9(4)°, 87.8(3)°, 103.58(6)°, 115.43(6)°, 94.7(3)° and 84.76(5)°, respectively. Thus, it showed a distorted square pyramidal geometry with *N,N'*-bidentate, two bridge bromides and one terminal bromide, achieving a five-coordinated complex. Note that the *xz*-plane of cyclopentyl rings in the *impy* of both complexes was distorted by approximately 90° with respect to the *xy*-plane of the pyridine ring and metal center.

[(*impy*)Cd(μ -Br)Br]₂ and [(*impy*)ZnCl]₂ were activated by modified methylaluminoxane (MMAO) to polymerise MMA, yielding PMMA with T_g 120 °C and 126 °C, respectively (Table 3). The triad microstructure [isotactic (*mm*, δ 0.85), atactic (*mr*, δ 1.02) and syndiotactic (*rr*, δ 1.21)] of PMMA was analysed using ¹H-NMR spectroscopy.⁵⁹ To confirm the catalytic activity of MMA polymerisation, blank polymerisation of MMA was performed with anhydrous CdCl₂, ZnCl₂ and MMAO at 60 °C, respectively. The catalytic activities of [(*impy*)Cd(μ -Br)Br]₂ (4.10 × 10⁴ gPMMA/molCd·h) and [(*impy*)ZnCl]₂ (2.07 × 10⁴ gPMMA/molZn·h)

were similar to the metal starting materials: CdCl₂ (3.53 × 10⁴ gPMMA/molCd·h) and ZnCl₂ (1.73 × 10⁴ gPMMA/molZn·h). Since the corresponding Pd(II) complex, [(*impy*)PdCl]₂, showed very high activity of 14.5 × 10⁴ gPMMA/molPd·h at 60 °C compared to reference complex PdCl₂ (1.97 × 10⁴ gPMMA/molPd·h)⁵⁴ thus, *impy*, which effectively generates an electron-rich cloud around the palladium metal and imparts steric hindrance in [(*impy*)PdCl]₂ to make an active species during MMA polymerisation, does not affect the Cd(II) and Zn(II) complexes. The syndiotacticity of PMMA was around 70%, which was similar to both Cd(II) and Zn(II) complexes and [(*impy*)PdCl]₂. Moreover, the moderate syndiotacticity was not sufficient to confer a coordination polymerisation mechanism for both Cd(II) and Zn(II) complexes and [(*impy*)PdCl]₂. Thus, we clearly did not observe steric or electronic effects of *impy* on cadmium and zinc metals in both of [(*impy*)Cd(μ -Br)Br]₂ and [(*impy*)ZnCl]₂ to improve the activity and syndiotacticity of MMA polymerisation.

In summary, the iminopyridyl-containing dimeric [(*impy*)-

Table 3. MMA polymerisation by [(*impy*)Cd(μ -Br)Br]₂ and [(*impy*)ZnCl]₂ in the presence of MMAO

Entry	Catalyst ^a	Temp (°C)	Yield ^b (%)	Activity ^c (g/mol-Cat·h) × 10 ⁴	T _g ^d (°C)	Tacticity			M _w ^e (g/mol) × 10 ⁵	M _w /M _n ^f
						%mm	%mr	%rr		
1	[CdCl ₂] ^g	60	22.6	3.53	123	5.60	30.3	64.1	4.72	1.49
2	[ZnCl ₂] ^g	60	11.1	1.73	129	9.20	24.2	66.6	1.33	1.58
3	[PdCl ₂] ^g	60	12.6	1.97	129	10.2	23.5	66.3	7.52	1.63
4	MMAO ^h	60	8.97	1.40	120	37.2	10.9	51.9	0.61	2.20
5	[(<i>impy</i>)PdCl] ₂ ⁱ	60	23.3	14.5	129	7.70	22.5	69.8	2.45	3.71
6	[(<i>impy</i>)Cd(μ -Br)Br] ₂	60	52.6	8.20	120	13.3	21.8	64.9	7.33	2.00
7	[(<i>impy</i>)ZnCl] ₂	60	13.2	2.07	126	7.90	20.6	71.5	7.67	2.02
8	[(<i>impy</i>)PdCl] ₂ ⁱ	25	1.09	3.63	130	7.90	17.8	74.3	1.38	3.09
9	[(<i>impy</i>)Cd(μ -Br)Br] ₂	25	1.92	0.30	110	20.0	26.0	54.0	0.65	1.84
10	[(<i>impy</i>)ZnCl] ₂	25	1.50	0.23	105	19.6	27.5	52.9	0.58	1.51

^a[M(II) catalyst]₀ = 15 μmol, and [MMA]₀/[MMAO]₀/[M(II) catalyst]₀ = 3100:500:1. ^bYield defined a mass of dried polymer recovered/mass of monomer used. ^cActivity is g of PMMA/(molM·h) at polymerisation temperature of 60 °C. ^dT_g is glass transition temperature which is determined by a thermal analyzer. ^eDetermined by gel permeation chromatography (GPC) eluted with THF at room temperature by filtration with polystyrene calibration. ^fM_n refers the number average of molecular weights of PMMA. ^gIt is a blank polymerisation in which anhydrous CdCl₂, ZnCl₂ and PdCl₂ were also activated by MMAO. ^hIt is a blank polymerisation which was done solely by MMAO. ⁱpolymerisation time was 0.5 h at 60 °C.⁵⁴

$\text{Cd}(\mu\text{-Br})\text{Br}_2$ and monomeric $[(\text{impy})\text{ZnCl}_2]$ have been prepared and structurally characterised. The coordination geometry around cadmium atom in $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}_2]$ and zinc in $[(\text{impy})\text{ZnCl}_2]$ showed a distorted square pyramidal and tetrahedral coordination, respectively. Both complexes have shown moderate catalytic activity for the polymerisation of MMA in the presence of MMAO with PMMA syndiotacticity characterized by ^1H NMR spectroscopy, which value was *ca.* 0.70.

Experimental

Materials and Instrumentation. $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$, anhydrous ZnCl_2 , picolinaldehyde, cyclopentylamine and methyl methacrylate (MMA) were purchased from Aldrich and anhydrous solvents such as $\text{C}_2\text{H}_5\text{OH}$, DMF, diethyl ether, dichloromethane were purchased from Merck and used without further purification. Modified methylaluminoxane (MMAO) was purchased from Tosoh Finechem Corporation as 6.9% weight aluminum of a toluene solution and used without further purification. Elemental analyses (C, H, N) of the prepared complexes were carried out on an elemental analyzer (EA 1108; Carlo-Erba, Milan, Italy). ^1H NMR (operating at 400 MHz) and ^{13}C NMR (operating at 100 MHz) spectra were recorded on a Bruker Advance Digital 400 NMR spectrometer; chemical shifts were recorded in ppm units (δ) relative to SiMe_4 as the internal standard. Electronic absorption spectra were obtained on an Ocean Optics USB4000 spectrophotometer (Ocean Optics, Dunedin, FL). Infrared (IR) spectra were recorded on Bruker FT/IR-Alpha (neat) and the data are reported in reciprocal centimeters. The molecular weight and molecular weight distribution of the obtained polymethylmethacrylate (PMMA) were carried out using gel permeation chromatography (GPC) (CHCl_3 , Alliance e2695; Waters Corp., Milford, MA). Glass transition temperature (T_g) was determined using a thermal analyzer (Q2000; TA Instruments, New Castle, DE).

Synthesis of Cd(II) and Zn(II) Complexes. *N*-Cyclopentyl-1-(pyridin-2-yl)methanimine ($[(N\text{-pyridin-2-ylmethylene})\text{cyclopentanamine}]$ (impy) was synthesized previously in the literatures.^{4,54,55}

***N*-Cyclopentyl-1-(pyridin-2-yl)methanimine(dichloro)-cadmium(II) bromide ($[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}_2]$).** A solution of impy (174 mg, 1.00 mmol) in anhydrous ethanol (10.0 mL) was added to a solution of $\text{CdBr}_2 \cdot 4\text{H}_2\text{O}$ (344 mg, 1.00 mmol) in dried ethanol (10.0 mL) at room temperature. Precipitation of white material occurred while stirring at room temperature for 12 hours. The white powder was filtered and washed with ethanol (25.0 mL \times 2), followed by washing with diethyl ether (25.0 mL \times 2) (0.790 g, 88.0%). The X-ray crystal of $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}_2]$ was obtained within three days from diethyl ether (10.0 mL) diffusion into an DMF solution (10.0 mL) of $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}_2]$ (50.0 mg). Analysis calculated for $\text{C}_{22}\text{H}_{28}\text{N}_4\text{Br}_4\text{Cd}_2$: C, 29.6%; H, 3.16%; N, 6.27%. Found: C, 29.8%; H, 3.20%; N, 6.26%. ^1H -NMR (DMSO- d_6 , 400 MHz) δ 8.86 (d, 2H, $J = 4.8$ Hz, $-\text{NC}_5\text{H}_4^-$), 8.64 (s, 2H, $-\text{N}=\text{CH}-\text{NC}_5\text{H}_4^-$), 8.19 (t, 2H, $J = 9.8$

Hz, $-\text{NC}_5\text{H}_4^-$), 7.98 (d, 2H, $J = 8.0$ Hz, $-\text{NC}_5\text{H}_4^-$), 7.78 (t, 2H, $J = 6.2$ Hz, $-\text{NC}_5\text{H}_4^-$), 4.11 (m, 2H, $-\text{C}_5\text{H}_9^-$), 1.93-1.86 (m, 8H, $-\text{C}_5\text{H}_9^-$), 1.73-1.57 (m, 8H, $-\text{C}_5\text{H}_9^-$). ^{13}C -NMR (DMSO- d_6 , 100 MHz) δ 159.42 (s, 2C, $-\text{N}=\text{CH}-\text{NC}_5\text{H}_4^-$), 150.15 (s, 2C, *ipso*- NC_5H_4^-), 147.76 (s, 2C, $-\text{NC}_5\text{H}_4^-$), 140.96 (s, 2C, $-\text{NC}_5\text{H}_4^-$), 128.47 (s, 2C, $-\text{NC}_5\text{H}_4^-$), 128.21 (s, 2C, $-\text{NC}_5\text{H}_4^-$), 70.13 (s, 2C, *ipso*- C_5H_9^-), 33.13 (s, 4C, $-\text{C}_5\text{H}_9^-$), 24.38 (s, 4C, $-\text{C}_5\text{H}_9^-$). IR (solid neat; cm^{-1}): 3086 (w), 2884 (w), 2806 (w), 2708 (w), 2614 (w), 2230 (w), 1941 (w), 1777 (s), 1650 (s), 1530 (s), 1444 (w), 1322 (s), 1172 (s), 1089 (s), 1017 (s), 932 (w), 861 (s), 774 (s).

***N*-Cyclopentyl-1-(pyridin-2-yl)methanimine(dichloro)-zinc(II) chloride ($[(\text{impy})\text{ZnCl}_2]$).** A solution of impy (87.0 mg, 0.500 mmol) in anhydrous ethanol (10.0 mL) was added to a solution of anhydrous ZnCl_2 (68.0 mg, 0.500 mmol) in dried ethanol (10.0 mL) at room temperature. Precipitation of white material occurred while stirring at room temperature for 12 hours. The white powder was filtered and washed with ethanol (25.0 mL \times 2), followed by washing with diethyl ether (25.0 mL \times 2) (0.150 g, 96.6%). The X-ray crystal of $[(\text{impy})\text{ZnCl}_2]$ was obtained within three days from diethyl ether (10.0 mL) diffusion into an acetone solution (10.0 mL) of $[(\text{impy})\text{ZnCl}_2]$ (50.0 mg). Analysis calculated for $\text{C}_{11}\text{H}_{14}\text{N}_2\text{Cl}_2\text{Zn}$: C, 42.5%; H, 4.54%; N, 9.02%. Found: C, 42.1%; H, 4.54%; N, 8.86%. ^1H -NMR (DMSO- d_6 , 400 MHz) δ 8.79 (d, 1H, $J = 3.6$ Hz, $-\text{NC}_5\text{H}_4^-$), 8.59 (s, 1H, $-\text{N}=\text{CH}-\text{NC}_5\text{H}_4^-$), 8.15 (t, 1H, $J = 3.8$ Hz, $-\text{NC}_5\text{H}_4^-$), 8.03 (d, 1H, $J = 7.6$ Hz, $-\text{NC}_5\text{H}_4^-$), 7.72 (t, 1H, $J = 7.4$ Hz, $-\text{NC}_5\text{H}_4^-$), 4.07 (m, 1H, $-\text{C}_6\text{H}_{11}^-$), 1.87-1.84 (m, 4H, $-\text{C}_5\text{H}_9^-$), 1.72-1.63 (m, 4H, $-\text{C}_5\text{H}_9^-$). ^{13}C -NMR (DMSO- d_6 , 100 MHz) δ 160.41 (s, 1C, $-\text{N}=\text{CH}-\text{NC}_5\text{H}_4^-$), 149.85 (s, 1C, *ipso*- NC_5H_4^-), 141.30 (s, 1C, $-\text{NC}_5\text{H}_4^-$), 128.61 (s, 1C, $-\text{NC}_5\text{H}_4^-$), 126.80 (s, 1C, $-\text{NC}_5\text{H}_4^-$), 110.77 (s, 1C, $-\text{NC}_5\text{H}_4^-$), 69.24 (s, 1C, *ipso*- C_5H_9^-), 33.42 (s, 2C, $-\text{C}_5\text{H}_9^-$), 24.54 (s, 2C, $-\text{C}_5\text{H}_9^-$). IR (solid neat; cm^{-1}): 3102 (w), 3024 (w), 2376 (s), 2313 (s), 2178 (w), 1750 (s), 1694 (s), 1649 (s), 1525 (s), 1217 (w), 1091 (s), 1023 (s), 944 (w), 775 (s), 713 (w), 643 (s).

Catalytic Activity for MMA Polymerisation. Methyl methacrylate (MMA) was extracted with 10% sodium hydroxide, washed with water, dried over magnesium sulfate, and distilled over calcium hydride under reduced pressure before use. To a 100-mL Schlenk flask containing $[(\text{impy})\text{Cd}(\mu\text{-Br})\text{Br}_2]$ (6.7 mg, 15 μmol) or $[(\text{impy})\text{ZnCl}_2]$ (4.7 mg, 15 μmol) in toluene (10.0 mL) was added MMAO (modified methylaluminoxane, 6.9 wt % in toluene, 3.25 mL, $[\text{MMAO}]_0/[\text{M(II) catalyst}]_0 = 500$) under a dry argon atmosphere. After the mixture had been stirred at 60 °C for 20 minutes, it was transferred into MMA (5.0 mL, 47.1 mmol, $[\text{MMA}]_0/[\text{M(II) catalyst}]_0 = 3100$). Then, the reaction flask was immersed in an oil bath at 60 °C and stirred for 2 hours. The resulting polymer was precipitated in methanol (400 mL) and HCl (3 mL) was added with stirring for 10 minutes. The polymer was filtered and washed with methanol (400 mL \times 3) to give poly methyl methacrylate (PMMA), which was vacuum-dried at 60 °C.

X-ray Crystallographic Studies. The crystal was picked

up with paratone-*N* oil and mounted on a Bruker SMART CCD diffractometer equipped with a graphite-monochromatic MoK α ($\lambda = 0.71073$ Å) radiation source and a nitrogen cold stream (200 K). Data collection and integration were performed with SMART and SAINT-Plus.⁵⁶ Semiempirical absorption corrections based on equivalent reflections were applied by SADABS.⁵⁷ The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL.⁵⁸ All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions.

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Supplementary Material. CCDC 985410 and CCDC 985411 contains the supplementary crystallographic data for [(impy)Cd(μ -Br)Br]₂ and [(impy)ZnCl₂], respectively. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- Chen, Z. F.; Tang, Y. Z.; Liang, H.; Fun, H. K.; Yu, K. B. *J. Coord. Chem.* **2006**, *59*, 207.
- Govindaswamy, P.; Mozharivskiy, Y. A.; Rao Kollipara, M. *Polyhedron* **2005**, *24*, 1710.
- Wang, W.; Spingler, B.; Alberto, R. *Inorg. Chim. Acta* **2003**, *355*, 386.
- Massa, W.; Dehghanpour, S.; Jahani, K. *Inorg. Chim. Acta* **2009**, *362*, 2872.
- Herrick, R. S.; Houde, K. L.; McDowell, J. S.; Kiczek, L. P.; Bonavia, G. *J. Organomet. Chem.* **1999**, *589*, 29.
- Schulz, M.; Klopffleisch, M.; Gorls, H.; Kahnes, M.; Westerhausen, M. *Inorg. Chim. Acta* **2009**, *362*, 4706.
- Shakhatareh, S.; Mohanraj, J.; Czapiak, A.; Tzimopoulos, D.; Kotoulas, S.; Gdaniec, M.; Akrivos, P. D. *J. Mol. Struct.* **2011**, *1002*, 51.
- Álvarez, C. M.; García-Rodríguez, R.; Miguel, D. *J. Organomet. Chem.* **2007**, *692*, 5717.
- Gonsalvi, L.; Gaunt, J. A.; Adams, H.; Castro, A.; Sunley, G. J.; Haynes, A. *Organometallics* **2003**, *22*, 1047.
- Buffin, B. P.; Squattrito, P. J.; Ojewole, A. O. *Inorg. Chem. Commun.* **2004**, *7*, 14.
- Vlček, A., Jr. *Coord. Chem. Rev.* **2002**, *230*, 225.
- Che, C.-M.; Huang, J.-S. *Coord. Chem. Rev.* **2003**, *242*, 97.
- Schoumacker, S.; Hamelin, O.; Pécaut, J.; Fontecave, M. *Inorg. Chem.* **2003**, *42*, 8110.
- Chavan, S. S.; Sawant, S. K.; Sawant, V. A.; Lahiri, G. K. *Inorg. Chim. Acta* **2010**, *363*, 3359.
- Kanas, D. A.; Geier, S. J.; Vogels, C. M.; Decken, A.; Westcott, S. A. *Inorg. Chem.* **2008**, *47*, 8727.
- Carmona, D.; Vega, C.; Lahoz, F. J.; Elipse, S.; Oro, L. A.; Lamata, M. P.; Viguri, F.; García-Correas, R.; Cativiela, C.; de VÍu, M. P. L.-R. *Organometallics* **1999**, *18*, 3364.
- Qiu, C.-J.; Zhang, Y.-C.; Gao, Y.; Zhao, J.-Q. *J. Organomet. Chem.* **2009**, *694*, 3418.
- Nienkemper, K.; Kotov, V. V.; Kehr, G.; Erker, G.; Fröhlich, R. *Eur. J. Inorg. Chem.* **2006**, 366.
- Datta, P.; Sarkar, S. K.; Mondal, T. K.; Patra, A. K.; Sinha, C. *J. Organomet. Chem.* **2009**, *694*, 4124.
- Roy, S.; Mondal, T. K.; Mitra, P.; Torres, E. L.; Sinha, C. *Polyhedron* **2011**, *30*, 913.
- Schnödt, J.; Manzur, J.; García, A.-M.; Hartenbach, I.; Su, C.-Y.; Fiedler, J.; Kaim, W. *Eur. J. Inorg. Chem.* **2011**, 1436.
- Braymer, J. J.; Choi, J.-S.; DeToma, A. S.; Wang, C.; Nam, K.; Kampf, J. W.; Ramamoorthy, A.; Lim, M. H. *Inorg. Chem.* **2011**, *50*, 10724.
- Álvarez, C. M.; García-Rodríguez, R.; Miguel, D. *Inorg. Chem.* **2012**, *51*, 2984.
- Zhang, J.; Li, W.; Bu, W.; Wu, L.; Ye, L.; Yang, G. *Inorg. Chim. Acta* **2005**, *358*, 964.
- Bose, D.; Banerjee, J.; Rahaman, S. H.; Mostafa, G.; Fun, H.-K.; Walsh, R. D. B.; Zaworotko, M. J.; Ghosh, B. K. *Polyhedron* **2004**, *23*, 2045.
- García-Tojala, J.; Rojo, T. *Polyhedron* **1999**, *18*, 1123.
- Gao, E.-Q.; Yue, Y.-F.; Bai, S.-Q.; He, Z.; Yan, C.-H. *Cryst. Growth Des.* **2005**, *5*, 1119.
- Lee, H. W.; Sengottuvelan, N.; Seo, H.-J.; Choi, J. S.; Kang, S. K.; Kim, Y.-I. *Bull. Korean Chem. Soc.* **2008**, *29*, 1711.
- Zhang, D.; Zhao, Z.; Wang, P.; Chen, X. *Bull. Korean Chem. Soc.* **2012**, *33*, 1581.
- Maldanis, R. J.; Wood, J. S.; Chandrasekaran, A.; Rausch, M. D.; Chien, J. C. W. *J. Organomet. Chem.* **2002**, *645*, 158.
- Johnson, L. K.; Mecking, S.; Brookhart, M. *J. Am. Chem. Soc.* **1996**, *118*, 267.
- Kettunen, M.; Vedder, C.; Brintzinger, H.-H.; Mutikainen, I.; Leskelä, M.; Repo, T. *Eur. J. Inorg. Chem.* **2005**, 1081.
- Ittel, S. D.; Johnson, L. K.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169.
- Johnson, L. K.; Killian, C. M.; Brookhart, M. *J. Am. Chem. Soc.* **1995**, *117*, 6414.
- Svejda, S. A.; Brookhart, M. *Organometallics* **1999**, *18*, 65.
- Small, B. L.; Brookhart, M. *J. Am. Chem. Soc.* **1998**, *120*, 7143.
- Small, B. L.; Brookhart, M. *Macromolecules* **1999**, *32*, 2120.
- Small, B. L.; Brookhart, M.; Bennett, A. M. A. *J. Am. Chem. Soc.* **1998**, *120*, 4049.
- Vedder, C.; Schaper, F.; Brintzinger, H.-H.; Kettunen, M.; Babik, S.; Fink, G. *Eur. J. Inorg. Chem.* **2005**, 1071.
- Tellmann, K. P.; Gibson, V. C.; White, A. J. P.; Williams, D. J. *Organometallics* **2005**, *24*, 280.
- Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. A.; Stromberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121*, 8728.
- Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.; Solan, G. A.; White, A. J. P.; Williams, D. J. *Chem. Commun.* **1998**, 849.
- Bianchini, C.; Mantovani, G.; Meli, A.; Migliacci, F.; Laschi, F. *Organometallics* **2003**, *22*, 2545.
- Gibson, V. C.; O'Reilly, R. K.; Wass, D. F.; White, A. J. P.; Williams, D. J. *Dalton Trans.* **2003**, 2824.
- He, X.; Yao, Y.; Luo, X.; Zhang, J.; Liu, Y.; Zhang, L.; Wu, Q. *Organometallics* **2003**, *22*, 4952.
- Bahuleyan, B. K.; Chandran, D.; Kwak, C. H.; Ha, C.-S.; Kim, I. *Macromol. Res.* **2008**, *18*, 745.
- Lian, B.; Thomas, C. M.; Casagrande, O. L., Jr.; Lehmann, C. W.; Roisnel, T.; Carpentier, J.-F. *Inorg. Chem.* **2007**, *46*, 328.
- Li, J.; Song, H.; Cui, C. *Appl. Organometal. Chem.* **2010**, *24*, 82.
- Wang, W.; Stenson, P. A.; Marin-Becerra, A.; McMaster, J.; Schroder, M.; Irvine, D. J.; Freeman, D.; Howdle, S. M. *Macromolecules* **2004**, *37*, 6667.
- Yang, M.; Park, W. J.; Yoon, K. B.; Jeong, J. H.; Lee, H. *Inorg. Chem. Commun.* **2011**, *14*, 189.
- Zhang, Z.; Cui, D.; Trifonov, A. A. *Eur. J. Inorg. Chem.* **2010**, 2861.
- Lansalot-Matras, C.; Bonnette, F.; Mignard, E.; Lavastre, O. *J. Organomet. Chem.* **2008**, *693*, 393.
- Kim, E.; Woo, H. Y.; Kim, S.; Lee, H.; Kim, D.; Lee, H. *Polyhedron*

- 2012**, *42*, 135.
54. Kim, S.; Kim, E.; Lee, H.-J.; Lee, H. *Polyhedron* **2014**, *69*, 149.
55. Dominey, R. N.; Hauser, B.; Hubbard, J.; Dunham, J. *Inorg. Chem.* **1991**, *30*, 4754.
56. SMART and SAINT-Plus v 6.22, Bruker AXS Inc., Madison: Wisconsin, USA, 2000.
57. Sheldrick, G. M. SADABS v 2.03, University of Göttingen: Germany, 2002.
58. SHELXTL v 6.10; Bruker AXS, Inc., Madison: Wisconsin, USA, 2000.
59. Kitaura, T.; Kitayama, T. *Macromol. Rapid Commun.* **2007**, *28*, 1889.
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